PADDING MADE FROM ADHESIVE COATED BEADS

RELATED APPLICATIONS

This patent application is a continuation-in-part of U.S. Patent Application Serial No. 09/506,507 filed February 17, 2000, which is a continuation-in-part of U.S. Patent Application Serial No. 09/226,311 filed January 7, 1999 (now U.S. Patent No. 6,032,300), which, in turn, is a continuation-in-part of U.S. Patent Application Serial No. 09/158,088 filed September 22, 1998 (now U.S. Patent No. 5,920,915).

BACKGROUND OF THE INVENTION

1. <u>Field of the Invention</u>. The invention disclosed herein generally relates to the field of breathable padding. More particularly, said invention relates to the field of breathable protective padding for impact absorbing sports gear and/or medical equipment that comes in prolonged contact with the human body (prosthetic devices, cushions, mattresses and the like).

2. <u>Discussion of the Background</u>. Designing protective padding for sports gear presents numerous challenges. In addition to having the padding perform its primary function of repeatedly absorbing high impact forces, such padding also should be lightweight, breathable, and washable. It also should be easily integrated into sports gear such as jerseys, pants, helmets, shoulder pads and the like - in a manner that does not unduly inhibit the user's movements.

Many prior art pads and padding techniques accomplish some of these goals - to varying degrees. For example, U.S. Patent No. 4,343,047 to Lazowski teaches use of loosely filled, lightweight beads

in a breathable casing to form a helmet pad. The helmet pad readily conforms to the contours of the wearer's head. In use, the loose beads are designed to move or shift around relative to each other within the casing. The beads also are designed to be crushable in order to absorb and attenuate particularly high impact forces. Crushable beads of this kind are designed to absorb one major impact, much like a car airbag. Therefore, padding made from crushable beads cannot be used in most athletic gear (e.g., football thigh and knee pads) since it must be able to withstand repeated impacts without losing its mechanical integrity.

Other prior art, sports-related, padding materials use incompressible beads that are designed not to be crushed (e.g., British Patent No. 1,378,494 to Bolton, U.S. Patent No. 3,459,179 to Olesen, and U.S. Patent No. 4,139,920 to Evans). Still others use beads that are resilient rather than crushable (e.g., U.S. Patent No. 3,552,044 to Wiele and U.S. Patent No. 5,079,787 to Pollman). These beads also are loosely packed in a bead containment sack or casing. Here again, this allows the beads to move, roll, flow, etc. relative to each other in order to achieve maximum pad conformation to the shape of a particular part of the human body. The Wiele patent further teaches lubrication of such beads to enhance their flowability to achieve such conformation. In this art, these loosely packed conditions are often referred to as "underfilling". The general object of underfilling is to achieve a padding material having the flow and conforming characteristics of a liquid-filled pad, without the burden of carrying the relatively heavy weight of liquids - or the need for waterproofing the casings needed to contain them.

While underfilled pads initially behave like a liquid when subjected to impacts, they have a tendency toward allowing the beads contained therein to be permanently driven out of the way in localized areas that receive repeated blows. This tendency gradually reduces the thickness of the padding around the human body part receiving

the repeated blows. Indeed, this tendency may even allow the human body part to eventually "bottom out" in the pad. Under such bottomed out conditions, the beads are driven away from the very areas where they are most needed.

Consequently, much of the padding used in today's athletic equipment is comprised of one or more sheets or layers of foam-like materials rather than underfilled pads. So used, these foam-like materials have the distinct advantage of not easily bottoming out. They also are relatively light in weight and inexpensive to manufacture. There are two general types of foam padding materials. The first type comprises so-called "closed cell" foams. Aside from not being inclined to bottom out, such foams also have the advantage of not absorbing moisture such as perspiration. However, closed-cell foams tend to be stiff – and, hence, body movement-stifling. Moreover, closed cell foam materials do not readily conform to human body contours, particularly under the rapidly changing conditions associated with many contact sports. Moreover, closed-cell foams do not "breathe" very well and therefore do not allow dissipation of the equipment user's body heat. Closed cell foams also suffer from the fact that they are not readily sewn into, or washable with, athletic clothing and equipment such as jerseys, pants and the like.

The second type of foam commonly used in sports and medical equipment comprises so-called "opened-cell" foams. These foams tend to be softer and more pliable than closed-cell foams. Hence, they tend to better conform to various contours of the human body, especially under rapidly changing conditions. They also do not inhibit the user's movements nearly as much as closed-cell foams. Open-cell foams also have good breathing qualities. Opened-cell foams do, however, tend to absorb and hold moisture and odor to such a degree that this tendency is often regarded as their major drawback. Hence, open-cell foams are usually coated with a waterproofing material (e.g., vinyl and the like) to prevent high levels of absorption of perspiration.

Unfortunately, use of these coating materials tends to make athletic pads made from opened-cell foams considerably less breathable and, hence, more body heat-retaining. Use of these coating materials also tends to make the underlying pads less pliable.

Padding materials made from polystyrene, polyethylene and polypropylene have proven to be especially efficacious in athletic equipment (e.g., football helmets, shoulder pads, etc.) that must repeatedly absorb impacts. The precursor beads (polystyrene, polyethylene, polypropylene and mixtures thereof) from which these materials are made are simply placed in a container and subjected to heat treatments (e.g., steaming) in order to join the individual beads to each other and thereby create unified materials from which padding for sports equipment can be made. These manufacturing processes are very generally depicted in Figures 1-6 of this patent disclosure. For example, the cross-sectional bead array shown in Figure 1 can be heated (e.g., by steam) in order to join or meld the individual beads 1, 2, 3, 4, 5, 6, etc. into a unified body of material such as that depicted in Figure 2. In Figure 1, the individual beads are shown having idealized, round configurations. This implies that void spaces will exist between abutting individual beads. Those skilled in this art will appreciate that these void spaces become filled in when the beads are made fluid or plastic in nature by the heat treatment used to join or meld the beads together in the manner suggested in Figure 2. After such heat treatments, the composite body constitutes a "foam" from which padding materials can be made. A perspective view of a generalized block of such foam material is depicted in Figure 3. It illustrates that the void spaces shown in Figure 1 become filled in (in all three dimensions) by the material from which the individual beads are made; hence the resulting foam material does not possess particularly good breathing qualities.

Other padding materials, that are primarily used in applications other than athletic equipment (e.g., building materials such as those

used in certain walls, doorways, flooring, tanks, etc.), have been designed to maintain void spaces between their individual beads even after they have been subjected to such heat treatments. The void spaces contribute to the relatively light weight of such building materials. Such materials are usually made from hollow microspheres or microbeads that are – to some degree – covered with a resin material that is applied to the microspheres by melting the resin material in the presence of the beads. For example, U.S. Patent 5,587,231 ("the '231 patent") teaches a foam material made from a mixture of hollow ceramic microspheres and dry granules of a resin powder. The dry resin powder is a thermosetting or high-temperature thermoplastic whose individual particles are mechanically mixed into a mass of dry microspheres. Upon heating the hollow microsphere/resin mixture to the resin powder's melting point, the microspheres become bonded together by a cured form of the resin that results from the heat treatment and subsequent cooling of the melted resin material. That is to say that the resin is in a melted state when it first goes into a liquid state (by virtue of having been melted) and makes its initial contact with the beads in this liquid (and melted) state. The end product material is an array of (1) hollow ceramic microspheres, (2) a thermally set resin that interconnects individual microspheres and thereby serves to hold said microspheres in a cohesive body and (3) void spaces. Optionally, the material may contain fiber strands as well. These materials are depicted in Figures 2A and 2B of the '231 patent as well as in Figure 11 of the present patent disclosure.

Because the dry resin powder taught in the '231 patent disclosure is simply mechanically mixed with the microspheres, the resulting materials are, to some degree, characterized by the fact that the cured resin does not tend to fully coat the microspheres (again see Figures 2A and 2B of the '231 patent or Figure 11 of the present patent disclosure). That is to say that the '231 patent's thermally set

resin material associates with the beads in such a manner that it generally serves to form branch-like, or net-like, components whose individual elements serve to interconnect the beads at certain limited locations on the bead's surface – as opposed to fully coating the microspheres. The '231 patent's end product materials also are characterized by the fact that the void spaces created by the thermal setting of the resin tend to be "clogged" and somewhat randomly created in said materials. Hence, the breathing qualities of these materials are not particularly good. This is, however, of little or no concern to the '231 patent disclosure because its light weight materials are intended for use as construction materials in buildings, aircraft, trucks, boats, tanks and the like. These breathing qualities will be contrasted with the padding materials of applicants' patent disclosure wherein the resulting bead/adhesive/void space materials remain highly breathable and hence better suited for use in athletic equipment or medical equipment.

U.S. Patent 5,888,642 ("the '642 patent") teaches a padding material similar to that taught in the '231 patent. It is comprised of microspheres that are held together in a coherent body by two resins. One of these resins is melted and subsequently thermally set. The teachings of this patent disclosure differ from those of the '231 patent in that the second resin in the '642 patent forms microballoons when suitably heated. In any case, the resulting material also has an array of hollow beads, resins and void spaces. It does not, however, necessarily have fiber strands as part of its make as in the case in the '231 patent. A representative material is shown in Figure 9 of the '642 patent and in Figure 11a of the present patent disclosure. As was the case in the '231 patent, the materials taught by the '642 patent are intended for use as construction materials rather than as padding for athletic equipment or medical equipment.

U.S. Patent 3,640,787 to Heller teaches a method of making construction materials from fully coating shaped beads of low specific

gravity (e.g., polystyrene) with a liquid binder material. In effect, the beads are first immersed in a liquid form of the binder. This immersion fully coats the beads. The resulting binder-covered beads are, in turn, coated with a solid pulverulent material such as particles of metal oxides, sand and the like. Figure 4 of the Heller patent disclosure shows that cell-like bodies are formed from the beads (e.g., polystyrene beads) and that the walls of these cells are comprised of the hardened binder material which also contains the pulverulent materials embedded therein. Since the resulting honeycomb-like materials have no void spaces between its adjoining cells, the resulting material does not have good breathing qualities. In other words, Heller's individual cells do have void spaces, but they are totally surrounded by the cell walls created from the beads and binder/pulverant coating on those cell walls. Here again, however, this is of little concern to the Heller patent disclosure since its end product materials also appear to be intended for use as building construction materials rather than padding for athletic equipment.

Thus, there remains a continuing need for padding materials that are particularly characterized by the fact that they are highly breathable, light in weight, conformable to the human body, not inclined toward absorption of perspiration and able to withstand repeated blows without mechanically breaking down and/or bottoming out. To this end, the padding materials disclosed herein have high levels of all of these desired qualities. Moreover, they can be easily incorporated into a wide variety of athletic equipment without unduly inhibiting the wearer's movements. They also are washable and relatively easy, and inexpensive, to make as well.

It might also be noted that, even though their ability to repeatedly absorb blows may not be needed, the other attributes of these padding materials (breathability, light weight, conformability to the human body) also make them well suited for use in medically related devices such as prosthetic devices, cushions, mattresses and

the like. Moreover, the breathing qualities of these materials may, alone, make them suitable for use as padding for certain goods that must be exposed to air during shipping. The breathability of these materials also makes them useful as filters. For example they would be particularly useful in equipment where both padding and filtering functions must be performed by the same material. By way of example only, applicants' materials can be used as padding in electrical equipment such as computer hard drive equipment that must be protected from mechanical disturbances and subjected to a stream of cooling air that must be filtered before introduced into hard drives that have very little tolerance for particles of foreign materials.

SUMMARY OF THE INVENTION

Applicants' padding materials are comprised of three dimensional arrays of beads that are held together in an air-porous, coherent body by an adhesive that substantially covers or coats a major portion (i.e., at least 50%, preferably at least 80% and most preferably, substantially 100%) of all of the beads in said coherent body. In order to do this, the adhesive will constitute from about 20 to about 80 weight percent of the padding material. Moreover, upon curing, the adhesive should have a hardness level ranging from about Shore A 20 to about Shore A 95. The resulting padding materials also should have void volumes that constitute from about 10 to about 40 volume percent of that material. The coated beads used to make these materials will generally have overall diameters (i.e., bead diameter plus coating thickness) ranging from about 1 to about 10 millimeters ("mm"). In some of the more preferred embodiments of this invention, however, these coated beads will have diameters ranging from about 1 to about 3 mm.

Applicants' substantial coating of these beads also is achieved by virtue of the fact that the adhesive is associated with the beads while said adhesive is in a liquid (or semi-liquid) state. This liquid state is not, however, brought about by melting said adhesive material(s). In other words, applicants' adhesive is not in a melted state when it is, as a liquid or semi-liquid, initially placed in contact with the beads. The adhesive is then cured or hardened from its initial liquid state (wherein the adhesive is not in a melted state) while in contact with said beads. Thus, for the purposes of this patent disclosure, expressions such as "adhesive cured from a liquid state (or semi-liquid state) wherein the adhesive is not melted while in contact with individual beads" means that applicants' adhesive compositions are not made to be liquids (or semi-liquids) by melting their adhesive components. This circumstance is to be contrasted with the teachings

of the '231 and '642 patents wherein beads are associated with dry resin particles which are first melted (and thereby become liquids or semi-liquids) and thereafter allowed to set in order to create the thereindisclosed bead/resin/void space systems.

Next, applicants note that, for the purposes of the present patent disclosure, the expression "substantially coats" should be taken to mean that an adhesive material covers at least 50 percent of a bead's surface area. Preferably, the majority of the beads in applicants' resulting padding materials will be at least 60% covered by an adhesive layer. More preferably, at least 80% of the beads in a given body of the padding materials of this patent disclosure will be at least 80% covered by such an adhesive material. Most preferably, substantially 100% of the beads will be substantially 100% covered with the liquid adhesive. To these ends, the liquid adhesive compositions of this patent disclosure will have viscosities ranging from about 500 centipoises ("cps") to about 5000 cps under ambient conditions. Generally speaking, the liquid adhesive composition will be capable of wetting the beads upon contact.

As was previously noted, the cured form of the adhesives employed in applicants' padding materials will have Shore hardness levels ranging from about Shore A 20 to about Shore A 95. In some of the most preferred embodiments of this invention, the Shore hardness levels of the cured adhesive coatings will range from about Shore A 60 to about Shore A 90. It also should be noted that, even after their volatile components have left the adhesive material as part of the curing process, the adhesive component of the end product material will represent a major part (20-80%) of the weight of the padding material even though it may represent a relatively minor part of the materials volume. Indeed, for reasons hereinafter more fully discussed, these adhesive materials will usually represent no more than about 5 volume percent of applicants' finished product padding materials.

The padding materials made according to the teachings of this patent disclosure also are particularly characterized by their possession of relatively large void volumes that are comprised of a large number of smaller void volumes that are, to a substantial degree, regularly spaced from each other. Moreover, these smaller void volumes are, to a large degree, in fluid communication with each other. This is to be contrasted with the totally encapsulated void volumes, if any, of the cells of the '787 patent disclosure (see Figure 4 thereof). The presence of an array of regularly spaced and greatly interconnected void volumes gives applicants' padding materials a particularly porous, breathable quality that greatly enhances their viability as athletic or medical equipment components. That is to say that the particularly good breathing qualities resulting from this array of regularly spaced void spaces that are in fluid communication with each other, produces improved perspiration evaporation and, hence, improved body heat dissipation, qualities in applicants' padding materials.

For purposes of this patent disclosure the expression "regularly spaced" should be taken to mean that (on average), at least one void space will preferably be present between at least every third bead (in all three dimensions). In some of the more preferred embodiments of this invention, this regularity will imply that such void spaces ideally will be present (on average) between every second bead. In some of the most preferred forms of applicants' padding materials, a void space will (on average) exist between substantially every bead in a body of said materials. The breathing qualities of applicants' padding materials generally tend to improve as this ideal is approached. Preferably, these void spaces will constitute at least about 10 percent, but no more than about 40 percent, of the total volume of the resulting padding material.

Applicants have found that the presence of these regularly spaced void spaces can be brought about when the adhesive is

applied in a liquid (or semi-liquid) state to the surface of the beads in quantities such that a subsequent dry form of the adhesive (resulting from its curing and/or drying) constitutes from about 20 weight percent to about 80 weight percent of applicants' end product, bead/adhesive/void space-comprised padding materials. In some of the most preferred embodiments of this invention the dried or cured form of the relatively hard adhesive will represent from about 40 to about 60 weight percent of applicants' end product padding materials.

Applicants' padding materials can be used alone, but in most cases involving sporting or medical equipment they will be placed in a pliable casing material such as a cloth-like, or web-like bag, casing or cover. When used in contact sports equipment, these padding materials (and their coverings) can be further associated with shell-like, outer facing, inelastic materials such as those hard plastic materials from which the outer surfaces of football helmets, football shoulder pads, thigh pads and the like are made. Some representative uses of applicants' padding materials in such equipment will be more fully illustrated in subsequent portions of this patent disclosure. Again, the porous, breathable, padding materials of this patent disclosure make them particularly well suited for use in athletic or medical equipment. They can, however, also be used when lightweight, shock absorption, or breathability are called for in other applications such as packaging materials for shipping other objects (such as mechanical or electrical equipment, fruit or vegetables), air filters, light weight building construction materials and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts (in cross section) a general array of prior art, foamable beads that are generally separated by void spaces 20.

Figure 2 depicts the result of heating the prior art foamable beads of Figure 1 (e.g., by steaming). In effect, the individual beads become, to some degree, melded or joined together by the heat treatment. That is to say that the beads 1, 2, 3, 4, 5, etc. shown in Figure 2 are no longer the distinctly round particles shown in Figure 1, but rather are partially melded or joined to one another in a manner that substantially fills in the void spaces 20 depicted in Figure 1.

Figure 3 depicts a three dimensional block of the material shown in Figure 2. Such a three dimensional block of material can be created by molding operations known to this art, or can be cut from slabs to desired shapes for use as padding materials including padding for athletic equipment.

Figure 4 depicts a prior art bead system similar to the one depicted in Figure 1. Figure 4 however shows some of the beads (i.e., beads 2, 3, 4, 5, 6 and 7) as being made of a material different from the remainder of the beads.

Figure 5 depicts the result of melding the beads shown in Figure 4 into a mixed bead system.

Figure 6 depicts a three dimensional block of the material shown in Figure 5. It should be specifically noted that the resulting materials shown in Figures 3 and 6 do not generally have distinct void spaces after the beads have been melded together by a heat treatment.

Figure 7 depicts a prior art system comprised of beads 1-19 that are held together in a coherent unit by a polymeric material 22. This polymeric material 22, in effect, fills in all of the void spaces between the various beads.

Figure 8 depicts a prior art system wherein a polymeric material 22 used to associate the beads 1-19 is employed in proportions such that the beads may be considered to be "immersed" in said polymeric material 22.

Figure 9 depicts a prior art system similar to that shown in Figure 7. It does however differ from the system shown in Figure 7 in that some of the beads are made from materials different from the remainder of the beads. For example, in Figure 9 beads 2, 3, 4, 5, 6 and 7 are depicted as being made from a material different from beads 1, and 8-19.

Figure 10 shows a prior art system similar to that shown in Figure 8 except for the fact that some of the polymeric material-immersed beads (i.e., beads 2, 3, 4, 5, 6, 7) are made of a material different from the material from which the remainder of the beads are made. All of the beads can be considered as being totally immersed in the polymeric material 22.

Figure 11 shows a prior art padding material (as taught by Figures 2A and 2B of the '231 patent) made from hollow ceramic microspheres that are held together in a coherent body by a resin material that interconnects the individual beads. The resulting material also has distinct void spaces 20 and fibers distributed throughout its structure.

Figure 11A shows a prior art padding material (as taught by Figure 9 of the '642 patent) made from hollow microspheres and two distinct kinds of resin – one of which forms microballoons when heated. This material has distinct void spaces 20.

Figure 12 depicts a basic component of the padding materials of the present patent disclosure. It shows a single solid bead 24 covered by a layer of adhesive material 26. The bead 24 can be made from an inelastic material or an elastic material.

Figure 13 depicts a two component bead that also can be used to make the hereindisclosed padding materials. The bead has an

inner, solid, bead 24 having a cover layer 24(a) of bead material that is different from the material from which the inner bead 24 is made. Thus, the resulting bead has two components 24 and 24(a) that each can be made of elastic or inelastic materials. This two component bead is shown about 50% covered with an adhesive layer 26 of varying thickness 27 (27').

Figure 14 depicts a solid bead having an ellipsoidal configuration that also can be used in the practice of this invention. Said ellipsoidal bead is shown about 80% covered with a layer of adhesive 26 of varying thickness 27".

Figure 15 shows a portion of an idealized, two dimensional, bead system wherein the beads are solid and wherein every third bead in this two dimensional presentation is regularly provided with an adjacent void space 20.

Figure 16 shows a portion of an idealized bead system wherein every second bead is regularly provided with an adjacent void space 20.

Figure 17 shows a portion of an idealized bead system wherein every bead is regularly provided with an adjacent void space 20.

Figure 18 depicts another two dimensional system of adhesive-coated beads associated in a manner taught by this patent disclosure. Said system is comprised of essentially round, solid beads (such as that shown in Figure 12) that are completely coated with a layer of adhesive material of substantially uniform thickness.

Figure 18A depicts an array of beads wherein some of the beads are not totally covered by the adhesive and wherein some of the bead bodies have, to some degree, melted together.

Figure 19 depicts an bead/adhesive/void padding material system of this patent disclosure that is comprised of uniformly coated beads made from three different bead construction materials and wherein some of the beads have holes passing through the body of the bead.

Figure 20 depicts an bead/adhesive/void space padding material of this patent disclosure that features the use of beads of different sizes and different construction materials as well as the use of non-coated beads in such padding materials.

Figure 21 illustrates the padding materials of the present invention integrated into various items of football equipment.

Figure 22 is a cross-sectional view of a pad made according to the teachings of this patent disclosure. Such pads can be used in various items of equipment for contact sports such as football, hockey, lacrosse and the like.

Figure 23 is an exploded view of a football thigh pad that employs the padding materials of this patent disclosure in conjunction with an outer facing shell made of a hard plastic material.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 12 depicts a basic building unit of one of the more preferred padding materials of this patent disclosure. This particular basic building unit is a solid bead 24 that is spherical in shape and substantially uniformly covered by a layer 26 of an adhesive material. This spherical configuration of the bead 24, and uniformly thick 25 adhesive coating 26, can be thought of as an "idealized" system. Those skilled in this art will however appreciate that commercially available beads may well have other configurations, idealized or otherwise (e.g., truncated spheres, ellipsoids, truncated ellipsoids, cubes, cylinders, tear drop shapes and the like). For example, several representative bead configurations that can be used in making applicants' padding materials are shown in a product brochure published by Porex Technologies Corp. (Fairburn, Georgia) entitled "Porex® Porous Plastics High Performance Materials" and said brochure is incorporated herein by reference. In some of the most preferred embodiments of this invention, these beads, no matter what their shape, will be made of materials that are subjected to one or more treatments (corona treatments in inert atmospheres, plasma jet treatments, flame treatments, etching, ozone treatments, etc.) to enhance the bonding qualities between the bead's outer surface and the adhesive layer placed on that outer surface.

Such beads can be made of inelastic materials or elastic materials. For the purposes of this patent disclosure the term "inelastic" can be taken to mean the bead's inability, upon deformation, to substantially return to its original shape. In other words, the material has no so-called "memory" as to its former (pre-deformation) shape. Conversely, the term "elastic" can be taken to mean a bead material having a memory, and hence the ability to return to its original shape after being deformed.

Whatever their shape, construction material, degree of elasticity or surface treatment experience, the beads of this patent disclosure generally will have (on average) a diameter D_1 (as measured on a bead's longest dimension – see for example D_1 of the ellipsoidal bead of Figure 14) ranging from about 1 mm to about 6 mm. Beads having average diameters ranging from 1 to 3 mm are, however, somewhat more preferred. It is even more preferred that the beads of this patent disclosure have average diameters ranging from about 1.5 to about 2.5 mm. In some of the more preferred embodiments of this invention, these beads, no matter their size, shape or method of manufacture will be made from plastic, ceramic, glass, plastic or phenolic resin materials in ways well known to those skilled in the bead making arts. By way of example only, a useful representative method for making round beads is taught in U.S. Patent 4,441,905 ("the '905 patent"). Hence, the teachings of the '905 patent are incorporated herein by reference. Other useful representative bead manufacturing methods are taught in U.S. Patents 4,989,794; 4,751,203; 4,751,202; and 5,292,840. Again, some of the most preferred resin compositions for the manufacture of applicants' beads will include polystyrene, polyethylene, polypropylene and especially ethyl propylene copolymers ("epps").

The bead 24 shown in Figure 12 is depicted, in cross section, as being a solid that is provided with a layer of adhesive material 26 that substantially uniformly coats the entire outer surface of the spherical bead 24. The thickness 27 of such a coating of adhesive material 26 preferably will range from about 5×10^{-6} mm to about 2 mm. Thus, upon curing of the adhesive, the overall diameter D_2 of the idealized, bead/adhesive layer system shown in Figure 12 will preferably range between about 1 mm and about 10 mm. Again, in some of the more preferred embodiments of this invention, the diameter of the beads will range from about 1 mm to about 3 mm. and the thickness of the adhesive layers coated thereon will range from

about $5x10^{-6}$ mm to about 2 mm. Hence, such fully coated beads may range in size (left side coating layer, plus bead diameter, plus right side coating layer) from about 1 to about 7 mm. Again, the adhesive layer placed on applicants' beads may be of substantially uniform thickness – or of varying thickness. To some degree, such uniformity will depend upon the method (auger mixing, spraying, immersion, etc,) by which the bead is coated.

Again, the solid, spherical bead 24 in Figure 12 is shown completely covered with a layer of adhesive 26 of substantially uniform thickness 25. This idealized circumstance is to be contrasted with the spherical, two-layered bead 24' shown in Figure 13 wherein said two layered bead 24' is only partially covered (e.g., about 50% of its surface area) by an adhesive layer 26' whose thickness 27, (27') is not uniform. That is to say that the adhesive layer 26' shown in Figure 13 has a greater thickness 27 on the far left end of the bead than its thickness 27' on its upper left side. The right side of the bead is shown having no adhesive coating whatsoever.

By way of another departure from the idealized bead/adhesive system depicted in Figure 12, Figure 14 illustrates, in cross section, an embodiment of this invention wherein the bead is an ellipsoidal solid 24". It is shown provided with a layer (of varying thickness) of adhesive 26 on about 80 percent of its surface area. Again, many different bead body configurations can be used in the practice of this invention (e.g., truncated spheres, truncated ellipsoids, cubes, bar-like configurations, cylinders, tear drop configurations and the like). This all goes to say that the coated beads of this patent disclosure may have a wide variety of geometric shapes (or mixtures of geometric shapes) so long as their longest dimension is between about 1 and about 10 mm. It might also be noted in passing here that this invention contemplates use of (1) different shaped beads, (2) different sized beads, (3) beads of different construction materials, (4) beads provided with varying thicknesses of different kinds of adhesive

materials, (5) solid beads, (6) hollow beads, (7) beads having holes through their bodies, (8) use of coupling agents to aid bead/adhesive bonding (e.g., use of titanates and silane for this purpose) and mixtures of beads having any combination of the just noted attributes (1) to (8) in the same padding material. It should also be noted that any of applicants' bead/adhesive systems may be improved upon by exposing the surfaces of the beads, whatever their shape, construction, material, etc. to various surface roughing treatments such corona plasma treatments (especially those carried out in inert gases such as argon, neon, etc. at pressures of about 10-20 torr), plasma jet, flame treatments, acid etching and/or ozone treatments and the like before they are coated with the adhesive. Such treatments generally serve to create stronger bonds between a given bead material and a given adhesive coating placed upon such a bead.

Figure 15 shows a system of four solid, coated beads (1, 2, 3 and 1') in an idealized, two dimensional, row-like, orientation. Those skilled in this art will appreciate that, in actuality, these beads will display the hereinafter described row-like features in a three dimensional sense. In any case, in Figure 15, the space between beads 1 and 2 is shown filled in with an adhesive material 26. Similarly, the space between beads 2 and 3 is shown filled in with adhesive material 26. The space between bead 3 and sequence repeating bead 1' is however shown as being a void space 20. Thus, it can be said that every third bead is provided with a void space. This is the preferred minimum requirement for the void spaces of the padding materials of the present patent disclosure to be considered as being "regularly spaced" as this term is used in this patent disclosure.

Figure 16 shows a more preferred embodiment of this invention wherein every second bead is regarded as being regularly provided with a void space. This is a more preferred form of "regular" spacing of the void spaces in applicants' padding materials. Figure 16 also shows an embodiment of this invention wherein bead 1 is a hollow

bead, bead 2 is a solid bead and bead 1' is a hollow bead. Thus the overall system can be regarded as a mixture of hollow and solid beads bound together according to the teachings of this patent disclosure. Those skilled in this art will, of course, appreciate that hollow beads also are well known to this art. For example, the previously cited '905 patent shows how hollow or solid beads can be made using various versions of the thereindisclosed technology. Moreover, the outer shells of applicants' hollow beads may be made of inelastic or elastic materials. Thus, the term "elastic" is not necessarily premised on the bead being hollow, but rather on the elastic nature of the bead forming material.

Figure 17 depicts a still more preferred embodiment of this invention where substantially every bead (e.g., beads 1, 2 and 1') is provided with a void space e.g., void spaces 20 in a three dimensional sense. This is the most preferred form of "regular" void spacing according to the teachings of this patent disclosure and to some degree represents a highly idealized embodiment of this invention.

Figure 18 shows a generalized system of another highly idealized bead/adhesive/void space system. The individual beads 1, 2, 3, 4, 5, 6 and 7 therein are shown to be solid in nature and substantially fully coated with respective, uniformly thick, layers of adhesive, i.e., layer 26(2) on bead 2, layer 26(3) on bead 3, etc. Thus, these beads can be thought of as being a part of a coherent, three dimensional, body by virtue of the fact that most of their respective adhesive coatings are in physical contact with – indeed melded with - the adhesive coatings of adjacent beads in that body. That is to say that the adhesive coatings of adjacent beads adhere to each other, in large part, by virtue of a bonding action between their originally liquid adhesive coatings. These coatings generally extend from the bead system's adhesive-to-adhesive contact or meld regions around a major portion of a given bead. Consequently, the beads are bonded to each other at the points of contact of their respective

adhesive coatings. For example, in Figure 18 bead 1 is bonded to the beads (1-7) by the adhesive-to-adhesive contact points 1(2), 1(3), 1(4), 1(5), 1(6) and 1(7). This adhesive-to-adhesive bonding action can be brought about by simply drying "wet", "liquid" (or "semi-liquid") or "tacky" adjoining adhesive coatings in ambient conditions. Such drying also can be accelerated by thermal or electromagnetic wave treatments of the wet or tacky adhesive coatings on adjacent coated beads.

In any case, applicants have found that such adhesive-to-adhesive bonds withstand impact type forces much better than bead-to-adhesive bondings or bead-to-bead bondings. Hence one of the underlying principles of this invention is to assure that a large percentage (e.g., at least 50%, preferably at least 80% and most preferably substantially 100%) of the beads are provided with such adhesive-to-adhesive bondings. This melding at their adhesive-to-adhesive contact points is preferably brought about by contacting the adhesive composition with the beads while said adhesive is at a temperature of about 20°F to about 200°F. Most preferably this contact will take place when the adhesive is at temperatures ranging from 50°F to 150°F. In any case, the adhesive-to-adhesive system created by these adhesive bonds becomes a subsystem within the overall bead/adhesive/void space system. Given the presence of this adhesive-to-adhesive system, impacts upon materials made from such a bead/adhesive/void space system are to a large degree distributed through the body of adhesive material coated on the outside surfaces of the coated beads.

As previously noted, a most important aspect of this invention also resides in the fact that the void spaces 20, 20', 20", etc. shown in Figure 18 exist between various subsets of the bead/adhesive system on the substantially "regular" bases previously described after the adhesives on adjacent beads have been bonded to each other. This regularly appearing void space system gives applicants' padding

materials those porous, breathable qualities that are especially desired in padding used in athletic or medical equipment. In other words, the drying or curing of the adhesive layers on the beads is such that the void spaces 20, 20', 20", etc. shown in Figure 18 are not substantially filled in with the adhesive material in the manner that the prior art bead systems depicted in Figures 7, 8, 9 and 10 of this patent disclosure are filled in with a polymeric material.

It also should be noted the applicants' void spaces are more regularly spaced than the void volumes 20 appearing in Figures 11 and 11(a). This regularity also tends to place applicants' void volumes in direct fluid communication with each other relative to the void volumes depicted in Figures 11 and 11(a). Again, the regularity and fluid communication in applicants' padding materials follows in large part from the fact that applicants contact their adhesives with their beads while the adhesive is in a liquid state that does not involve melting of the adhesive components of applicants' formulations. Again, by way of contrast, the bead/resin/void space systems depicted in Figures 11 and 11(a) are produced by melting dry resin particles while they are in the presence of the hollow microbeads of that material.

Applicants also have found that the presence of such substantially regularly spaced void spaces (in three dimensions) can be so created when the amount of adhesive coated upon (e.g., by auger mixing, spraying, immersion, etc.) a given amount of beads represents from about 20 weight percent to about 80 weight percent of the resulting padding materials of this patent disclosure. More preferably, applicants' adhesive/total padding material weight ratio will be such that the adhesive will represent from about 40 to about 60 weight percent of a given end product padding material. That is to say that such weight ratios will exist after the adhesive has fully dried or cured to an extent such that virtually all of its volatile components have departed.

By way of an example of the effects of changes in the amounts of adhesives used in these formulations, applicants determined that when beads (solid or hollow beads, made from inelastic or elastic materials) having diameters ranging from about 1 mm to about 6 mm are coated with an amount of adhesive that upon drying or curing, constitutes about 40 weight percent of the resulting padding materials, at least about 50% of the beads have surface areas that are at least about 50 percent covered with the said adhesive. Such padding materials also will have void volumes of from about 10 to about 40 volume percent of the total volume of the resulting padding material i.e., the volume of the overall bead/adhesive layer/void volume system. When however, the same beads described in the previous example were mixed with an amount of adhesive that, upon drying, constituted about 50 weight percent of applicants' end product materials, about 90% of the resulting adhesive coated beads will have surface areas that are at least 80 percent covered with the adhesive and the void volume of the materials still falls well within the lower end of desired 10-40 volume percent level. Applicants also would note in passing that adhesive percentages (50-60 weight percent) that produce void volumes of about 30 to 35 volume percent are somewhat more preferred in the practice of this invention.

Applicants also have established that there is an upper limit to this adhesive/bead weight ratio. Generally speaking, applicants have determined that if a padding material otherwise made by the teachings of this invention is comprised of more than about 80 weight percent (or more than about 5 volume percent) of adhesive, the void volume of that padding material becomes, in effect, "filled in" by the adhesive. Such circumstances are generally depicted in the prior art related Figures 7-10 of this patent disclosure. Thus, these prior art figures also depict "excessive" use of the adhesive according to the teachings of the present patent disclosure. Again, this follows from the fact that the resulting padding material loses one of its most important

attributes – its breathability – when its void spaces are filled in by the adhesives. Hence, applicants prefer to use their adhesive materials in amounts such that the void spaces in the resulting material will represent at least about 10 percent of the padding material's entire volume. Padding materials having void volumes ranging from about 30 to about 40 volume percent of the total volume of the resulting padding material are even more preferred. To this end, applicants have found that the adhesives in applicants' padding materials (in the adhesive's cured form) will, most preferably, constitute no more than about 60 weight percent of the end product padding material.

Many of applicants' more preferred padding materials use adhesives that are far more dense than the bead materials. For example, in one particularly preferred polystyrene/adhesive formulation used in the practice of this invention, applicants found that use of 1% (by vol.) more of the adhesive produced a 25% gain in the weight of the resulting padding material. Use of 2% (by vol.) more adhesive produced a 39% increase in the padding material's weight. Similarly, use of 3% (by vol.) more adhesive led to a 48% increase in weight while use of 4% (by vol.) more adhesive usage produced a 55% weight gain in the end product material.

Applicants also found that use of more than about 5% (by volume) of adhesive in the padding materials of this patent disclosure produced end products having rather poor breathing qualities. That is to say that applicants have found that use of more than about 5 volumes percent adhesive in the padding material of this patent disclosure tends to clog or fill in the void volumes to such a degree that they lose much of their breathing qualities. It might also be again noted that the higher densities of the adhesives relative to the beads used in the practice of this invention are such that the above noted 5% by volume adhesive generally corresponds to a padding material comprised of about 80% by weight adhesive. Thus, applicants' invention calls for the use of adhesive components that represent from

about 10 to about 80 weight percent of the resulting padding material. This range generally corresponds to use of about 1 to 5 volume percent adhesive in the padding materials of this patent disclosure.

Figure 18A depicts a departure from the idealized bead/adhesive/void space system shown in Figure 18. Beads 1, 2 and 7 in Figure 18A are shown in circumstances wherein these three beads are not completely covered by a uniform layer of adhesive. Moreover, bead 7 is shown partially melded into the bodies of beads 1 and 2. Thus, beads 1, 2 and 7 are associated with each other by this melding of the bead material rather than by the melding of an adhesive coating on the contact regions of these particular beads. In effect, the void space 20" shown in Figure 18 has been filled in by the partially melded bodies of beads 1, 2 and 7 depicted in Figure 18A. Moreover, bead 7 is no longer attached to bead 6. Figure 18A is employed to show that occasional occurrences of this bead-to-bead melding can be tolerated in applicants' padding materials to some degree. It can not however predominate. Thus, in the more preferred embodiments of this invention, the remaining void volume of applicants' padding material shown in Figure 18A (i.e., void spaces 20, 20', etc.) should still constitute at least 10 volume percent of the padding materials of this patent disclosure. That is to say that even if some bead-to-bead melding has taken place (and, hence, filled in void volumes such as that depicted by item 20" of Figure 18) this bead-to-bead melding will not take place to such an extent that the void volume of the padding material will be less than about 10 volume percent.

Figure 19 depicts another idealized bead/adhesive/void space system made according to the teachings of the present invention wherein the beads are of the same size, but are not made of the same material. For example, beads 1 and 8-19 are depicted as being made of a material different from the remainder of the beads. Moreover, beads 2, 4 and 6 are depicted as being made from materials different

from beads 3, 5 and 7. Moreover, some of these beads may be hollow (e.g., beads 10, 13, 16 and 19) while others are solid. Moreover, some of these solid beads may have holes passing through their otherwise solid bodies (see for example, beads 11, 14 and 6). These holes may allow air to pass through some of the beads and thereby add to the breathability of the overall padding material. It also should be noted that regardless of whether the beads are solid, hollow or solids having holes they can be made of inelastic materials while others are made of elastic materials. The resulting system should, however, still be characterized by the presence of regularly spaced void spaces 20, 20', 20", etc. that constitute at least about 10 volume percent of the material and by the fact that all of the adhesive-coated beads in this mixed bead type system will have average diameters ranging from about 1 mm to about 10 mm.

Figure 20 depicts a bead/adhesive/void space padding material of this patent disclosure wherein some of the beads are of different sizes. Moreover, some of these different-sized beads are solid while others are hollow and while still others are depicted as being made of materials different from the remainder of the beads. Solid bead 4 is shown having a hole 4(1) passing through its diameter region. The same is true of bead 11 which has a hole 11(1) passing through its diameter region. Bead 13 has two such holes 13(1) and 13(2) passing through its bead body. The bead/adhesive/void space system shown in Figure 20 also indicates that some of the beads (e.g., beads 3, 9 and 10) are not covered by any adhesive coating. Preferably less than 20 percent - and more preferably less than 10 percent (by weight), and most preferably less than 5 percent (by weight) - of the beads in a given padding material of this patent disclosure will fail to be at least 50 percent coated with an adhesive.

In any case, those skilled in this art also will appreciate that by blending beads of various sizes, the volume of the individual voids or interstitial spaces can be varied. By way of example, the void spaces

20' and 20" shown in Figure 20 are shown to be considerably larger than the "idealized" void volumes 20, 20', 20" etc. shown in Figure 18. Those skilled in this art also will appreciate that the idealized void volumes 20, 20', 20", etc. shown in Figure 18 represent about 26 volume percent of the idealized, theoretical system depicted in Figure 18 wherein all of the spherical beads are assumed to be of a uniform size. Thus, the spaces 20' and 20" shown in the bead system of Figure 20 represent the means by which applicants' padding materials can have void volumes that are greater than, or less than, the theoretical 26 volume percent of the idealized system shown in Figure 18. For example, if the relatively large void spaces 20' and 20" shown in Figure 20 were of such relative sizes, the resulting padding material could have a void volume greater than the theoretical 26 volume percent of the system shown in Figure 18. On the other hand, if the relatively large void spaces 20', 20" in Figure 20 are to a large degree filled in with the adhesive material, the void volume of the resulting system can be less than the theoretical 26 void volume percent of the idealized system of Figure 18. Again, the adhesives used to make applicants' padding materials are used in quantities (to weight percent of the resulting padding material) such that the void volumes of applicants' padding materials will range from about 10 to about 40 volume percent with void volumes of about 30 to 35 volume percent being somewhat more preferred.

Applicants have found that one simple, straightforward method by which the adhesive-to-adhesive bonding action, bead/adhesive weight ratio and void space requirements can be achieved is by mixing the liquid adhesive with the beads in an auger type mixing and conveying device known to those skilled in this art. In effect the liquid adhesive is accurately metered into an auger-driven flow of the dry beads in order to thoroughly mix and blend the liquid adhesive with the dry beads at the required ratios. In any case, the end result of applicants' construction methods is that adjacent beads within a given

body of the padding material will remain in substantially fixed positions relative to each other after the adhesive coating materials on the beads bond with each other. Consequently, the pads of the present invention will be highly breathable, impact resistant and will not bottom out under the influence of repeated blows.

Representative Uses of Padding Materials

Figure 21 represents some representative uses of the padding materials of the present invention wherein said padding materials are especially adapted for use in various items of football gear. Other sports gear or sports gear components can of course be made from the hereindisclosed padding materials. Such materials also are well suited for use in medical equipment such as prosthetic devices, wheelchair cushions, mattresses and the like. And as previously noted, the qualities of light weight, impact resistance and breathability make these materials well suited as padding in certain, non-human body-related/usages such as padding for mechanical equipment, padding for perishable goods (e.g., eggs, fruit, etc.) and air (or other gas) filter materials. Be that as it may, the football gear shown in Figure 21 includes a liner jersey 28 with upper arm 30, rib 32, and sternum 34 pads. Such gear also can include liner pants 36 with thigh 38 and knee 40 pads as well as a helmet 42 with head pads 44 and 44'. Liner gear such as jersey 28 and pants 36 can be worn by a football player right next to the body. External gear such as full shoulder pads and exterior or playing jerseys and pants can be worn over such liner gear. Such exterior gear also can be similarly padded with materials made according to the teachings of the present invention. It should of course be appreciated that applicants' padding materials can be easily adapted for use in many other types of sports padding devices including separate and removable pads such as the elbow 46 and forearm 48 pads depicted in Figure 21.

Figure 22 is a cut-away view of the elbow pad 46 of Figure 21 employing padding material made according to the teachings of this invention wherein a coated bead 52/void space 54 material is placed in an outer casing 56. The outer casing 56 is preferably made of a cloth-like or net-like material that is porous and breathable (e.g., plastic mesh or net of a substantially waterproof material such as polypropylene). In use, the entire pad 46 can be received or sewn into a pocket 50 formed by portions 58 and 60 of the jersey 28 depicted in Figure 21.

Figure 23 shows a padding material 62 made according to the teachings of this patent disclosure placed in two distinct casing sections 64 and 64'. These casing sections 64 and 64' are each associated with an outward facing, hard plastic cover 66 that is connected to the casing sections 64 and 64' by means of rivet-shaped connectors 68. Such a system could be used as a thigh pad, rib pad and the like.

Bead Construction Materials

The beads of this invention can be made of various materials e.g., plastics, ceramics (including glass), metal oxides, phenol based resins, etc. For example, in the "plastics" group, expanded ethylene, polystyrene and polypropylene are preferred bead construction materials for both elastic and inelastic bead materials. Ceramic, glass and metal oxide are somewhat preferred construction materials for the inelastic beads of this patent disclosure. One method for producing ceramic beads is described in U.S. Pat. 4,239,519 ("the '519 patent"). For example, the '519 patent teaches how gels containing 5 to 6% solids will form ceramic-forming droplets that consistently have a spherical shape. Beads made from ceramic materials may, however, also be somewhat resistant to those treatments (etching, corona treatments, etc.) that often effect better bead/adhesive bonding in

other bead construction materials such as the previously noted plastics.

Plastics and resins are preferred for making elastic and/or hollow beads that can be used in applicants' padding materials. Such plastics are generally made from resins through the application of heat, pressure, or both. Such resin materials generally fall into two broad categories: (1) *thermoplastic resins*, which can be heated and softened innumerable times without suffering any basic alteration in characteristics; and (2) *thermosetting resins*, which, once set at a temperature critical to a given material, cannot be resoftened and reworked. Thermoplastic resins and thermosetting resins have the advantage of readily accepting corona, flame, plasma jet and etching treatments.

The principal kinds of thermoplastic resins that can be used to make the beads of this invention include: (1) acrylonitrile-butadiene-styrene resins; (2) acetals; (3) acrylics; (4) cellulosics; (5) chlorinated polyethers; (6) fluorocarbons, polytetrafluoroethylene; polychlorotrifluoroethylene, and fluorinated ethylene propylene; (7) nylons (polyamides); (8) polycarbonates; (9) polyethylenes (including copolymers); (10) polypropylenes (including copolymers such as ethyl propylene copolymers ("epps")); (11) polystyrenes; and (12) vinyls (polyvinyl chloride). The principal kinds of thermosetting resins that can be employed to make the inelastic beads suitable for the practice of this invention include: (1) alkyds; (2) allylics; (3) the aminos (melamine and urea); (4) epoxies; (5) phenolics; (6) polyesters; (7) silicones; and (8) urethanes.

As previously noted in this patent disclosure, applicants have defined "inelastic" beads as those that will not recover to their original shape after an impact or extended compression. By use of the term "inelastic", applicants mean that a bead material has what is commonly referred to as poor "memory". Hence, after deformation, such materials will not return to their original shape and will not retain

much of their original impact attenuation properties. In effect, many individual beads in such a system are permanently crushed. It might be noted in passing here that applicants' test for material elasticity was to place a 0.5 inch piece of a subject foam under a device which compressed the foam at ambient conditions to 50 percent of its original thickness. The pressure was then released. By way of example only, after 30,000 compression cycles of this test, applicants noted only a 10 to 15 percent reduction in thickness in certain elastic polyethylene foams and a 20 to 25 percent reduction in thickness for certain elastic polypropylene foams. Similarly tested inelastic foams however remained substantially at their compressed thicknesses indefinitely.

Adhesive Materials

The adhesives that can be employed in the practice of this invention are generally characterized by the fact that they (1) can be placed in solution or suspension (colloidal or otherwise) in liquid (or semi-liquid) carrier fluids (polar, non-polar, organic, inorganic) known to this art and (2) will cure to hardness levels of Shore A 20 to shore A 95. The carrier fluids used to convey such adhesive materials should be capable of acting as a carrier for a particular adhesive material components of applicants' adhesive compositions as well as being capable of wetting the surface of the bead material being employed to make a given padding material. Beyond that, the adhesive components of applicants' carrier/adhesive systems may be broadly classified into two main groups; organic and inorganic. The organic adhesives can be subdivided into those of animal origin, vegetable origin, and synthetic origin. Other useful classifications for those adhesives that can be used to make the hereindescribed padding materials are based upon the chemical nature of the adhesive. Such chemical classifications usually comprise (1) protein or protein derivatives, (2) starch, cellulose, or gums and their derivatives, (3)

thermoplastic synthetic resins, (4) thermosetting synthetic resins, (5) natural resins and bitumens, (6) natural and synthetic rubbers, and (7) inorganic adhesives.

Two part thermoplastic or thermosetting adhesive systems are somewhat preferred for the practice of this invention. They usually consist of a resin and a hardener. The resin typically has a polyol or bulk polymer component. The hardener causes this polymer to link up, chain extend, harden and/or cure. Those skilled in this art will appreciate that the term "resin" typically refers to the base stock used in an adhesive. With less preferred, but still operable, single component adhesives, the resin will have most, but not all, of the bonding power of the final product.

Thermoplastic synthetic resin adhesives comprised of a variety of polymerized materials such as polyvinyl acetate, polyvinyl butyral, polyvinyl alcohol, and other polyvinyl resins; polystyrene resins; acrylic and methacrylic acid ester resins; cyanoacrylates; and various other synthetic resins such as polyisobutylene, polyamides, coumarone-indene products, and silicones also can be employed in the practice of this invention. Other thermosetting synthetic resin adhesives that can be used in the practice of this invention will include phenol-aldehyde, urea-aldehyde, melamine-aldehyde, as well as certain condensation-polymerization materials such as furane and polyurethane resins. Adhesive compositions containing phenol-, resorcinol-, urea-, melamine-formaldehyde, phenolfurfuraldehyde, and the like also can be used in the practice of this invention.

The adhesive containing compositions of this patent disclosure also may contain such additives as tackifiers, viscosity modifiers, anti-oxidants, UV inhibitors, UV stabilizers, catalysts, heat stabilizers, oxygen scavengers, colorants, biocides, odorants, etc. It might also be noted in passing that applicants have found that Dibutyl Tin Dilaureate (a general purpose organo-tin catalyst) used at 0.075% loading (a 1:1333 catalyst to adhesive ratio), can serve as a

particularly good adhesive curing catalyst. In all such variations, however, the cured form of the adhesives should have Shore A values ranging from about 20 to about 95. Adhesives having hardness levels (in their cured state) ranging from about Shore A 50 to a Shore A value of about 90 are even more preferred in the practice of this invention when used in conjunction with inelastic thermosetting or high temperature thermoplastic bead materials. Those cured adhesives having hardnesses levels ranging from about a Shore A 60 to about Shore A 85 are even more preferred for use with such beads.

Some of the more preferred, commercially available, adhesives that can be used in the practice of this invention, and their relative attributes, are as follows:

Adhesive	Qualitative properties
Rubinate 9272®	Low hardness, low strength, high flexibility, high elongation, moisture curing polyurethane. Especially good for soft bead products.
Rubinate 9234®	High hardness, high strength, brittle, moisture curing polyurethane. Especially good for hard bead products.
Rubinate 9457®	Medium high hardness, medium high strength, fair flexibility and elongation. Good for medium hard bead or hard bead products requiring some flexibility.

Experimental Findings Re: Impact Tests

Applicants' experimental findings have established that, when used in the hereindescribed proportions (20-80 wt. %, or 1-5 vol. %), certain adhesives (those having hardness levels ranging from about Shore A 20 to Shore A 95) play an important part in the ability of the hereindisclosed bead/adhesive/void space padding materials to repeatedly absorb high levels of impact energy. This finding was primarily established through use of various impact tests. For example, in one series of such impact tests (so-called Acceleration Peak (G) tests) whose results are shown below as Test 1 below, applicants kept the percent of adhesive constant at 2 volume percent

and varied the "hardness" of the adhesive. This variation in hardness was accomplished by increasing the number of chemically active sites of the adhesives by adding varying amounts of a second chemically active component to a base resin system. For example in polyurethane formulations, the relative amount of a N=C=O component of the adhesive was varied relative to a NH-C-NH component of said adhesive. Such tests indicated that as the hardness of the adhesive material used to create the subject bead/adhesive/void space materials of this patent disclosure was increased, the material's impact absorptive ability increased as well. These tests also indicated that the adhesive itself (and not just the beads) contributes greatly to the impact absorption qualities of applicants' padding materials.

For example, line 1 of Test 1 shows that when the subject padding material employs beads designated as bead type 3420 (spherical, high density, polypropylene beads) and uses 2% (by vol.) of a "soft" adhesive designated as 9272, the Acceleration Peak (G) value ("AP(G) value") is 107 - for the first impact upon that material. This 107 AP(G) value represents good impact resistance for this material – on the first impact. The second impact (see line 2 of Test 1), however, produced an AP(G) value of 272. This value indicates a substantial lessening or deterioration in the impact resistance of the material whose attributes are given in line 1. The third impact (line 3) produced an AP(G) value of 465. This value indicates that the padding material's impact resistance greatly deteriorated under the three impacts to a level (465) which is such that the material would not be considered an acceptable padding for high impact sports gear.

Line 4 of Test 1 shows that when the padding material employs the same bead (3420) and the same volume (2%) of a "harder" adhesive (adhesive 9457), under otherwise comparable test conditions, the AP(G) value for the first hit was 95. This 95 value is qualitatively "better" than the 107 value for the padding material

described in line 1, i.e., the padding material of line 4 is a better padding material than the material described in line 1 – under the first impact. The second impact upon the padding material described in line 4 produced an AP(G) value of 182 (see line 5 of Test 1). This 182 value is better than the 272 value produced by the second hit on the material described in line 1. Similarly, the third hit upon the material of line 4 produced a 266 AP(G) value which is much better than the 465 value for the third hit upon the material of line 1. Thus, these tests show that the harder adhesive (9457) produces better repeated blow impact resistance in padding materials of this type relative to the softer adhesive (9272).

Lines 8 and 9 of Test 1 show the results of a series of tests comparable to those described above. The spherical bead employed (bead 3419) was, however, considerably softer than the bead employed (bead 3420) in the previous tests. A padding system using this softer bead (3419) and the softer adhesive (9272) as indicated in line 8 of Test 1 produced a first impact AP(G) value of 493. By way of comparison, the padding system using the softer, bead (3419) and the harder adhesive (9457) described in line 4 of Test 1 produced a first impact value of 297. Thus, use of the harder adhesive (9457) improved the impact resistance of a padding material employing softer beads (3419).

Lines 10 and 11 of Test 1 show similar improved results from use of the harder adhesive (9457) relative to the softer adhesive (9272) in a system wherein the beads had a cylindrical configuration rather than spherical configurations of the beads used in all of the other tests described above. Thus, applicants have concluded that the shape of the beads was not responsible for the improved results obtained through use of harder adhesives such as adhesive 9457.

Test 2 shows the results of another series of tests wherein Acceleration Peak (G) values were determined for various padding material wherein the effects of changes in the volume percentage of a

soft adhesive (9272) on the AP(G) values of the material were studied. Test 2 also explores the effects of comparable changes in the volume percentage of a hard adhesive (9457) on AP(G) values of the resulting material. For example, line 1 of Test 2 describes a padding material employing beads designated as 3420 (again, spherical, hard beads made of polypropylene). Line 1 shows that use of 2 volume percent of soft adhesive (9272) adhesive produced a AP(G) value of 110. Impact number 2 on this same material produced an AP(G) value of 254 (see line 2 of Test 2) and impact number 3 produced a 383 value (see line 3 of Test 2).

Line 4 of Test 2 describes a padding material comparable to that described in line 1 except for the fact that the padding material described in line 4 uses 3% of the soft adhesive (9272). This material produced a first impact AP(G) value of 103, a second impact value of 209 and a third impact value of 317. Each of these three AP(G) values represent a modest gain over the comparable values produced by the 2% soft adhesive systems described in lines 1 to 3 of Test 2.

The results of comparable impact tests on a padding material employing 4% of the soft adhesive (9272) generally indicates that the material has lost some of its impact resistance (see lines 7 and 8) relative to the first two impacts on both the 2% and 3% soft adhesive systems. The third impact test on the 4% soft adhesive system (see line 9) shows some improvement (342 v. 383) over the third impact results of the 2% adhesive material. It also shows some loss in impact resistance (342 v. 317) relative to the third impact on the 3% soft adhesive containing padding material. The 5% soft (9272) adhesive containing material described in lines 10 to 12 shows AP(G) values that are, in most cases, modest improvements over the 2%, 3% and 4% adhesive materials.

The Test 2 results beginning at line 14 show the results of impact tests comparable to those just described – except for the fact that the line 14-35 tests employed a hard adhesive (9457) rather than

the soft adhesive (9272) previously described with respect to the test described in lines 1-13 of Test 2. For example, lines 14-16 of Test 2 show AP(G) values for the first three impacts upon a hard bead (3420)/2% hard adhesive (9457) system to be 90, 177 and 252. Each of these AP(G) values is lower (and therefore "better") than the comparable values produced by the 2% soft adhesive (9272) system described in lines 1 to 3 of Test 2. Lines 18-20 of Test 2 show that the AP(G) values (i.e., 83, 151 and 220) for the first three impacts on the 3% hard adhesive (9457) are better than those for the 3% soft adhesive (i.e., 103, 209 and 317). Moreover, the fourth, fifth and sixth hits on the 3% hard adhesive material suggest that the added impacts are having less and less destructive effects. The 3% hard adhesive values for the first three hits are also better than the comparable values for the 2% hard adhesive (i.e., 90, 177 and 252). The AP(G) values for first three impacts on the 4% hard adhesive (i.e., 90, 136 and 161) also are better than those for the 4% soft adhesive (i.e., 114, 264 and 342). The 4% hard adhesive (9457) values also are generally better than the 2% and 3% hard adhesive systems. Moreover, the fourth, fifth and sixth impacts produce AP(G) values (i.e., 197, 214, 228) that suggest that the bad effects of repeated blows is reaching a plateau in the 4% hard adhesive system.

The first three AP(G) values for the 5% hard (9457) adhesive (i.e., 92, 134 and 160) of Test 2 are much better than those for the 5% soft adhesive (i.e., 105, 208 and 289). They are, however, only marginally better than the results of the first three impacts on the 4% hard adhesive material. The 5% hard adhesive system does, however, produce better results (i.e., 182, 203 and 209 AP(G) values) with respect to the fourth, fifth and sixth impacts. Thus, it would appear that the impact resistance of these padding materials is reaching a plateau when the adhesive constitutes about 5 value percent of the padding material. As was previously noted, this 5 volume percent for the adhesive in the overall padding material

generally corresponds to about 80 weight percent of the padding material owing to the fact that the adhesives are normally much more dense than the beads. Moreover, applicants have generally found that the use of more than about 5 volume percent adhesive (or more than about 80 weight percent adhesive) tends to clog or fill in the void volumes of applicants' padding materials to the point where their desired breathing qualities are greatly impaired. Again, applicants prefer that their padding materials have void volumes of at least 10% of the volume of the material. Again, applicants have found that when more than 5 volume percent (or 80 weight percent) adhesive is used, the void volume usually falls below about 20 volume percent of the material. Hence, for reasons of breathability, as well as diminishing returns with respect to impact resistance, applicants prefer to use no more than 80 weight percent (and preferably less than 60 weight percent) adhesive in the padding materials of this patent disclosure.

TEST 1

	Bead	Vol. % adhesive	Test Temp	Size (thickness)	Melt Point	Drop Ht.	Accel Peak (G)
1	3420	2% 9272	122deg. F	1"	275deg. F	.86m	107
2							272
3							465
4	3420	2% 9457	122deg. F	1"	275deg. F	.86m	95
5							182
6							266
7							379
8	3419	2% 9272	122deg. F	1"	275deg. F	.86m	493
9	3419	2% 9457	122deg. F	1"	275deg. F	.86m	297
10	Cylindrical	2% 9272	122deg. F	1"	329deg. F	.86m	327
11	Cylindrical	2% 9457	122deg. F	1"	329deg. F	.86m	146
12							486

TEST 2

	BEAD CODE	BEAD MATERIAL	BEAD DENSITY (pcf)	% adhesive	UT CODE (HELMET #)	SAMPLE THICKNESS	CONDITION	IMPACT LOCATION	ANVIL	DROP HEIGHT (M)	ACCELERATION PEAK(G)
1	3420	epp	3.5	2%9272	BR0301	1"	hot	OT	flat	0.86	110
2	3420	epp	3.5	2%9272	BR0301	1"	hot	OT	flat	0.86	254
3	3420	epp	3.5	2%9272	BR0301	1"	hot	OT	flat	0.86	383
4	3420	epp	3.5	3%9272	BR0302	1"	hot	OT	flat	0.86	103
5	3420	epp	3.5	3%9272	BR0302	1"	hot	OT	flat	0.86	209
6	3420	epp	3.5	3%9272	BR0302	1"	hot	OT	flat	0.86	317
7	3420	epp	3.5	4%9272	BR0303	1"	hot	OT	flat	0.86	114
8	3420	epp	3.5	4%9272	BR0303	1"	hot	OT	flat	0.86	264
9	3420	epp	3.5	4%9272	BR0303	1"	hot	OT	flat	0.86	342
10	3420	epp	3.5	5%9272	BR0304	1"	hot	OT	flat	0.86	105
11	3420	epp	3.5	5%9272	BR0304	1"	hot	OT	flat	0.86	208
12	3420	epp	3.5	5%9272	BR0304	1"	hot	OT	flat	0.86	289
13	3420	epp	3.5	5%9272	BR0304	1"	hot	OT	flat	0.86	379
14	3420	epp	3.5	2%9457	BR0305	1"	hot	OT	flat	0.86	90
15	3420	epp	3.5	2%9457	BR0305	1"	hot	OT	flat	0.86	177
16	3420	epp	3.5	2%9457	BR0305	1"	hot	OT	flat	0.86	252
17	3420	epp	3.5	2%9457	BR0305	1"	hot	OT	flat	0.86	357
18	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	83
19	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	151
20	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	220
21	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	229
22	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	277
23	3420	epp	3.5	3%9457	BR0306	1"	hot	OT	flat	0.86	278
24	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	90
25	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	136
26	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	161
27	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	197
28	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	214
29	3420	epp	3.5	4%9457	BR0307	1"	hot	OT	flat	0.86	228
30	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	92
31	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	134
32	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	160
33	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	182
34	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	203
35	3420	epp	3.5	5%9457	BR0308	1"	hot	OT	flat	0.86	209

It is counterintuitive that a harder, and presumably more brittle, adhesive material would be a better impact absorbing material than a softer, more elastic adhesive. Nonetheless, this is the case in applicants' bead/adhesive/void space padding materials. Applicants have made many tests such as Tests 1 and 2 and have concluded that some form of micro-fracturing of the adhesive, and perhaps even certain kinds of beads, takes place during impact and that this micro-fracturing can greatly contribute toward the impact absorbing quality of these padding materials.

While applicants' invention has been described with respect to various theories, specific examples, and a spirit that is committed to the concept of coating certain sized beads with a layer of hard adhesive in order to produce padding materials having improved breathability and impact resistance, it is to be understood that this invention is not limited thereto, but rather only should be limited by the scope of the following claims.